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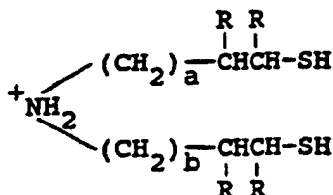
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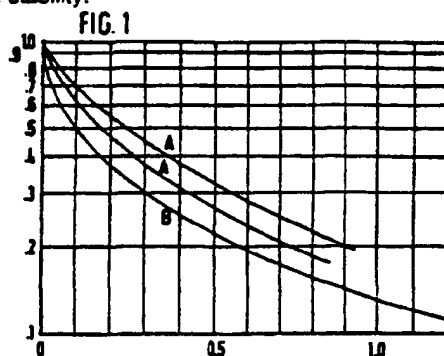
(54) Process and catalyst for production of a bisphenol.

(57) The invention relates to a process for preparing a bisphenol comprising contacting at least two moles of a phenol per mole of a ketone in the presence of a sulphonated cation-exchange resin having a plurality of sulphonic acid sites ionically-bound to a group of the formula:



in which each of a and b is an integer from 0 to 5 and each R individually represents H, OH, SH or alkyl. The catalyst exhibits high activity and selectivity at moderate reaction temperatures, low production of colored impurities, and high stability.

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Bispheno-A (BPA), an important base chemical used as a starting material for polyepoxide and polycarbonate resins, is commercially prepared by reacting phenol and acetone in the presence of an acidic catalyst such as sulphuric acid, hydrochloric acid or a sulphonic acid cation-exchange resin. Cation-exchange resins offer the advantage, over free acid catalysts, of safer and more convenient handling. For certain applications such as polycarbonate production, it is particularly important to produce BPA which has extremely high purity, particularly with respect to impurities which add colour to the BPA. Efforts have been made to improve the quality of the BPA product and the efficiency of the BPA process by modifying the catalyst.

Various mercaptan group-containing materials have been used as such chemically-bonded promoters for cation-exchange resin catalysts, including alkyl mercaptoalcohols (U.S. Patent Specification 3,049,568), C₂-C₄ alkyl mercaptoamines (U.S. Patent Specification 3,394,089) and N-aminoorganomercaptan groups (U.S. Patent Specification 4,584,416). Since both the catalyst acidity and the presence of mercaptan groups are factors in the effectiveness of the catalyst, the one-for-one exchange of sulphonic acid sites on the ion-exchange resin for mercaptan groups represents a compromise of catalyst efficiency. It would be desirable to have ion-exchange resin catalysts for BPA production which are highly active at moderate reaction temperatures, highly selective, not subject to degradation under typical reaction conditions, and capable of producing BPA low in coloured impurities.

According to the invention, BPA is prepared by the reaction of acetone and phenol in the presence of a polyfunctional mercaptoamine-modified cation-exchange resin catalyst. The catalyst is characterized by at least partial substitution of the ion-exchange resin with an alkylmercaptoamine group having at least two alkylmercaptan branches. The catalyst is preferably prepared by the mercaptoamine addition to the sulfonyl groups of a cation-exchange resin.

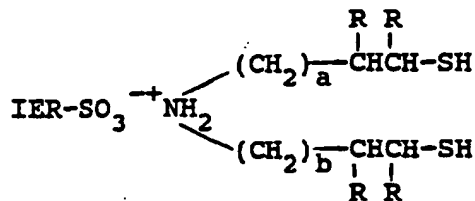
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impurities and good stability.

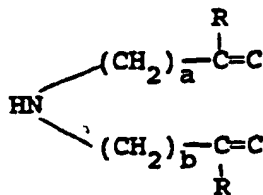
The invention catalyst can be described by the formula:



in which IER represents the backbone of an ion-exchange resin, each of a and b is an integer from 0 to 5 and each R is selected independently from H, OH, SH and alkyl groups. The ion-exchange resin can be any insoluble strong-acid cation-exchange resin, preferably an aromatic sulphonic acid resin having a cation-exchange capacity of at least about 0.5 and preferably at least 2.0 meq/g dry weight. Particularly suitable are strong acid sulfonated styrene-divinylbenzene copolymer resins. Such ion-exchange resins are commercially available in gel and macroreticular form as, for example, Dowex 50 resins, Amberlite IR resins, Dowex MSC-1 resins, Amberlyst 15 resins and Duolite C-20 resins (Dowex, Amberlite, Amberlyst and Duolite are registered trade marks). The catalyst is suitably employed as 0.15-1.3 mm (15-100 mesh) resin beads in a fixed bed.

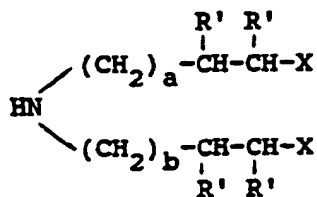
The commercially-available aromatic sulphonic acid resins are generally handled as sodium salts. These acid salts are preferably converted to the acid form by conventional means prior to treatment with the chosen aminomercaptan modifying agent.

The preparation of the aminomercaptan modifier can be carried out by firstly halogenating a diolefinic amino compound of the general formula:



in which a, b and R are as described above, and then reacting the reaction product of the first step with sodium thioacetate and hydrolysis.

Diolefinic amino compounds include, for example, the diallylamine in which a and b are 1. Alternately, the modifier can be prepared by starting with a secondary amine containing multiple alkyl halides of the general formula:



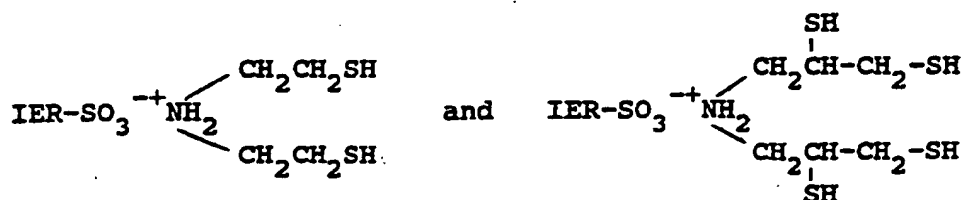
in which R' is selected independently from H, Cl, Br, I and alkyl groups, and each X is independently chosen from Cl, Br and I. Such compounds include, for example, the bis-2-haloethylamine. The above halogen-containing amine salt, for example the bis-2-halogenethyl amine hydrochloride salt, is reacted with sodium thioacetate in an alcoholic medium such as ethanol. The resulting bis-(2-thioacetyethyl)acetamide can be acid neutralized by hydrolysis and reacted with sulphonyl groups of the cation-exchange resin by reflux together in aqueous alcoholic solution with an optional reducing agent such as triphenyl phosphine.

The modified resin is then washed with an aqueous alcohol in solution and dried in a vacuum at 50 °C to 100 °C.

The currently preferred modified cation-exchange resin catalysts of the invention can be described by the formulas:

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The modified ion-exchange resin catalyst will generally have from 2 mole per cent to 50 mole per cent of chemically-modified sulphonic acid units, preferably 3 to 25 mole per cent.

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The invention catalyst is useful in the preparation of a bisphenol by the reaction of a ketone, such as acetone, ethyl methyl ketone, isobutyl methyl ketone, acetophenone, cyclohexanone, 1,3-dichloroacetone and the like, with a phenol such as phenol, o-cresol, m-cresol, o-chlorophenol, m-chlorophenol, o-t-butylphenol, 2,5-xyleneol, 2,5-di-t-butylphenol, o-phenylphenol and the like. The commercially-significant utility of the catalyst is in the reaction of acetone with phenol to prepare bisphenol-A. In the cation-exchange resin-catalyzed preparation of BPA, an excess of phenol, generally 5 to 20 moles per mole of acetone, is desirable for high acetone conversion. The condensation reaction is carried out at temperatures in the range of 30 °C to 120 °C, preferably 45 °C to 100 °C. The reaction is generally carried out under atmospheric pressure. Solvents or diluents are not necessary except at low reaction temperatures. The reaction can be carried out in batch or continuous form. The modified cation-exchange resin catalyst can be used as a slurry with the reactants in batch reactions or in a fixed bed in a continuous process.

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The reaction time depends upon the reaction temperature and other reaction conditions. In a batch process, a reaction time within the range of 0.5 to 20 hours will generally achieve desired conversion. In a continuous operation using a fixed catalyst bed, a flow rate within the range of 0.1 to 12.0, preferably 0.5 to 6, weight per hour per bed weight will generally be suitable. The product mixture is then separated from the catalyst, and the BPA can be recovered by means such as flash distillation to remove water, phenol and other volatile impurities. Purification of the BPA can be effected by distillation, recrystallization, solvent washing, and the like.

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Carrying out the production of BPA in the presence of the modified sulphonic acid exchange resin described herein results in a BPA product having a low level of coloured impurities. The catalyst is highly active and stable at reaction temperatures of below about 100 °C and has been found to exhibit high activity at reaction temperatures as low as 65 °C.

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The following examples illustrate preparation of exemplary modified catalysts and use of the invention modified catalysts in the preparation of BPA.

Example 1

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This example illustrates preparation of bis-2-(thioacetylethyl)acetamide and subsequent in-situ modification of a cation-exchange resin with the bis(2-mercaptoethyl)amine.

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Sodium thioacetate was prepared by adding slowly 349.21 g of sodium ethoxide-ethanol solution (at 14.88 %w solution) into 58.05 g of distilled thioacetic acid in an ice bath under nitrogen atmosphere. 367.94 g of the above solution was then added to 320.16 g of a bis[2-chloroethyl]-amine hydrochloride/ethanol solution (12.5 %w solution) under nitrogen atmosphere. The well-mixed reaction mixture was heated and refluxed for about 45 minutes. The resulting slurry was filtered, and the filtrate was subjected to vacuum distillation at temperatures below 80 °C to remove most of the solvent.

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164.77 g of reagent grade acetone was added to the cooled residue to dissolve the product and precipitate additional salt. After a second filtration, the filtrate was vacuum distilled at below 60 °C to remove volatiles. 56.71 g of final product residue having 5.17 %w nitrogen content based on Kjeldahl analysis was recovered.

10.16 g of the reaction product from step 1, 146.20 g of wet DOWEX (registered trade mark) MSC-1, 74.64 g of methanol and 895.36 g of deionized water were charged into a 2 litre flask equipped with stirrer,

condenser and thermometer. The mixture was heated to reflux for 7 hours. After standing overnight, the slurry was washed/filtered with deionized water, methanol and deionized water several times. 157.33 g of wet product resin catalyst was recovered. Analysis showed 13.5 %w and 15.7 %w of sulphur on the starting and product resin catalyst, respectively.

- 6 The wet resin catalyst was dried in a vacuum oven (at about 70 °C for 24 hours) when used for batch reactions, or used as wet resin in continuous reactions. In the latter case, the dry feed serves to remove moisture as well from the invention resin catalyst during the initial purge period.

10 Example 2

- This example illustrates the preparation of bis-2,3-(dihalidepropyl)amine hydrochloride salt. 128.6 g of bromine was slowly added to a mixture of 53.7 g of diallylamine hydrochloride and 402.6 g of methylene chloride in a 1 litre flask with nitrogen blanketing. The system temperature was controlled to 10-20 °C in an ice water bath. Upon completion of bromine addition, the slurry mixture was further allowed to mix at room temperature overnight, and product was separated from the mother liquor, washed with additional methylene chloride and dried. The product was titrated with silver nitrate at room temperature. Total free halide found was 2.087 meq/g (theory: 2.206 meq/g).

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Example 3

- This example shows the results in terms of product properties in a batch reaction using the invention modified ion-exchange resin catalyst and compares the product with those from processes in which other catalysts are used. The invention processes (G-1, G-2, MR-1) were carried out with catalysts made according to Example 1. The reaction conditions included a phenol to acetone ratio of 12:1 molar, a 2:1 weight ratio of catalyst to acetone, and a reaction temperature of 70 °C. Results are tabulated in Table 1. Although generalizations are difficult from batch data, the invention bis-(2-mercaptoethyl)amine-modified catalyst generally exhibits superior selectivity for the p,p' isomer, compared with the cysteamine-modified catalyst, and essentially equivalent reactivity under batch conditions.

Example 4

- This example compares the activity and performance of the invention modified cation-exchange resin catalyst B and a cysteamine-modified catalyst A. The invention catalyst was a Dowex (registered trade mark) MSC-1 cation-exchange resin modified by 10% substitution with bis-(2-mercaptoethyl)amine (BMEA) and the comparison catalyst was a Dowex MSC-1 cation-exchange resin modified by 12% substitution with cysteamine groups ($\text{NH}_2\text{CH}_2\text{CH}_2\text{SH}$). Continuous runs were performed at 70 °C using a phenol to acetone ratio of 12:1.

- Figure 1 compares acetone conversion, a measure of catalyst activity, for the two catalysts in a continuous BPA preparation process. In Figure 1 is given on the vertical axis the 1 minus conversion (1-conversion) value expressed in a number and on the horizontal axis the reciprocal value of the weight hourly space velocity, expressed in h (hours). Figure 1 illustrates the activity of the BMEA-modified catalyst over a two-week period, versus the activity of the cysteamine-modified catalyst over a two-week period, with declining with time. The lowest line A represents the values for the first week, the other line A for the second week. The results show the superior activity and stability of the invention catalyst B.

- In Figure 2 is given on the vertical axis the (1 minus conversion) value and on the horizontal axis the p,p'-BPA divided by 0,p'-BPA selectivity expressed in a number. Figure 2 shows the presence of by-products in the reaction product mixture for the invention catalyst compared with the cysteamine-modified catalyst. Use of the BMEA-modified catalyst resulted in higher p,p'/o,p' selectivity (Figure 2). In general, the BMEA-modified catalyst under continuous reaction conditions exhibits superior performance in terms of selectivity, stability and BPA colour, while the cysteamine catalyst appeared to yield marginally lower levels of two common BPA by-products of uncertain identity.

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TABLE 1

Cat.	Modifier	% Modifier	% p,p' BPA	% o,p' BPX	% BPX	% Codimer (Impurity)	% Conv (Basis acetone)	% Conv (Basis BPA)	% Conv by recovery
G-1 ²	NH(CH ₂ CH ₂ SH) ₂ (ionic)	10.8	18.0	0.50	0.09	0.01	83.7	95.5	96
MR-1	NH(CH ₂ CHSHCH ₂ SH) ₂ (ionic)	10.0	12.7	0.35	0.05	0.02	65.3	68.3	56
G-2 ¹	NH(CH ₂ CH ₂ SH) ₂ (ionic)	13.6	14.1	0.40	0.09	---	84.6	77.5	---
MR-2	Non-modified	0	4.3	0.65	0.03	0.25	19.3	27.6	17
MR-3	Free CO ₂ HCH ₂ CH ₂ SH	14.0	16.0	0.36	0.09	0.02	92.2	98.9	20 ³
G-3 ²	Non-modified	0	9.8	1.43	0.14	0.43	81.0	63.5	---
MR-4	Cysteamine (ionic)	21.0	11.2	0.24	0.08	0.01	62.7	61.0	58
G-4 ¹	Non-modified	0	10.3	1.20	0.08	0.50	64.8	63.8	38
G-5 ²	Free CO ₂ HCH ₂ CH ₂ SH	14.0	24.6	0.72	0.13	0.04	97.9	> 100.0	114 ³
G-6 ¹	Free CO ₂ HCH ₂ CH ₂ SH	14.0	18.1	0.58	0.13	0.05	> 98.0	98.8	76 ³
G-7 ²	Cysteamine (ionic)	10.0	15.2	0.53	0.08	0.03	89.7	82.9	---
G-8 ¹	Cysteamine (ionic)	30.6	14.2	0.34	0.08	0.01	71.2	76.6	81

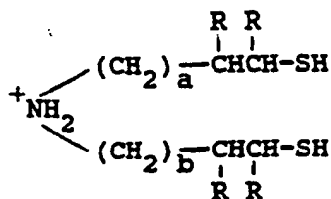
1. 4% crosslinked divinylbenzene

2. 2% crosslinked divinylbenzene

3. Stripping free acidic mercaptan results in product degradation and inconsistent results.

Claims

1. A process for preparing a bisphenol comprising contacting at least two moles of a phenol per mole of a ketone in the presence of a sulphonated cation-exchange resin having a plurality of sulphonic acid sites ionically-bound to a group of the formula:

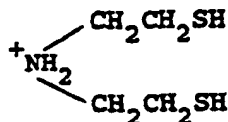


in which each of a and b is an integer from 0 to 5 and each R individually represents H, OH, SH or alkyl.

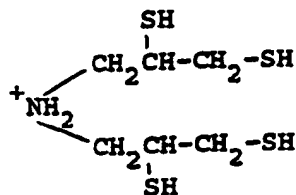
2. A process according to claim 1 in which the cation exchange resin has at least 2 mole per cent of the sulphonic acid sites modified by the ionically-bound group.

3. A process according to claim 2 in which 3 to 25 mole per cent of the sulphonic acid sites of the cation-exchange resin are modified by the ionically-bound group.

4. A process according to claims 1-3 in which the cation-exchange resin has the sulphonic acid sites modified by the group of the formula:



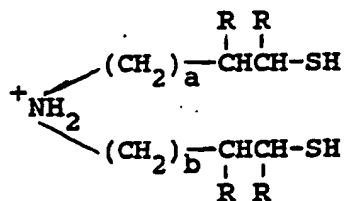
5. A process according to any one of the claims 1-3 in which the cation-exchange resin has the sulphonic acid sites modified by the group of the formula:



6. A process according to any one of the claims 1-5 in which the cation-exchange resin is a sulphonated styrene-divinylbenzene copolymer resin.

7. A process as claimed in any one of the claims 1-6 in which the bisphenol is bisphenol-A, the phenol is phenol, and the ketone is acetone.

8. A sulphonated cation-exchange resin having a plurality of the sulphonic acid sites ionically bound to an aminomercaptan group of the formula



10 in which each of a and b is an integer from 0 to 5 and each R individually represents H, OH, SH or alkyl.

9. A cation-exchange resin according to claim 8 in which from 3 to 25 mole per cent of the sulphonic acid sites is modified.

10. A cation-exchange resin according to claim 8 or 9 in which the backbone is styrene-divinylbenzene copolymer.

FIG. 1

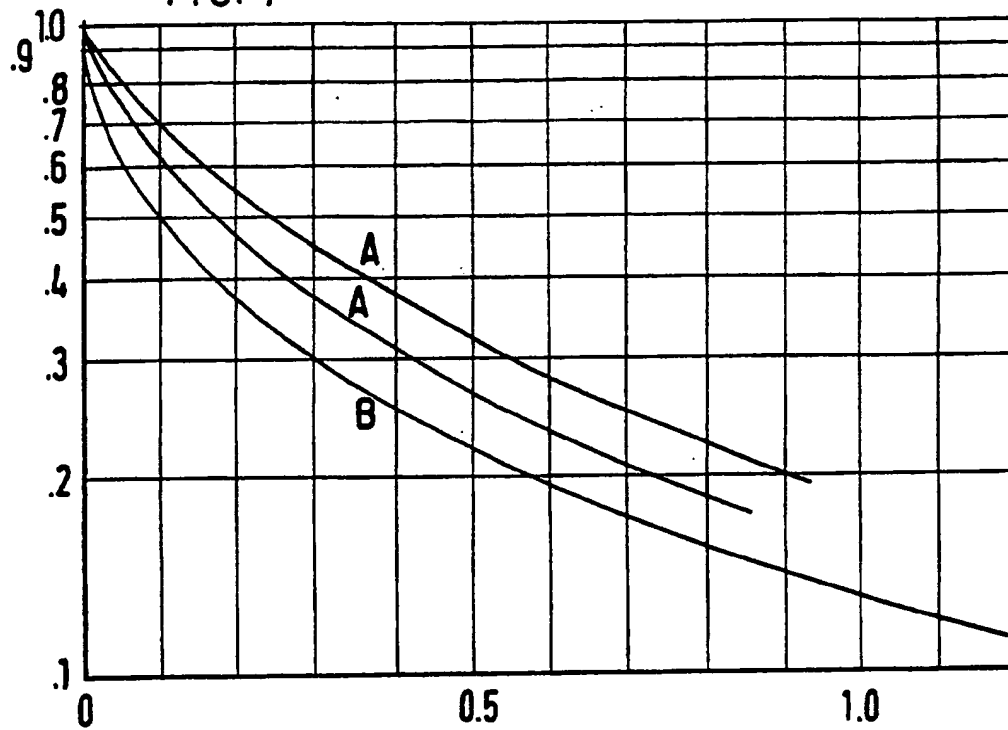
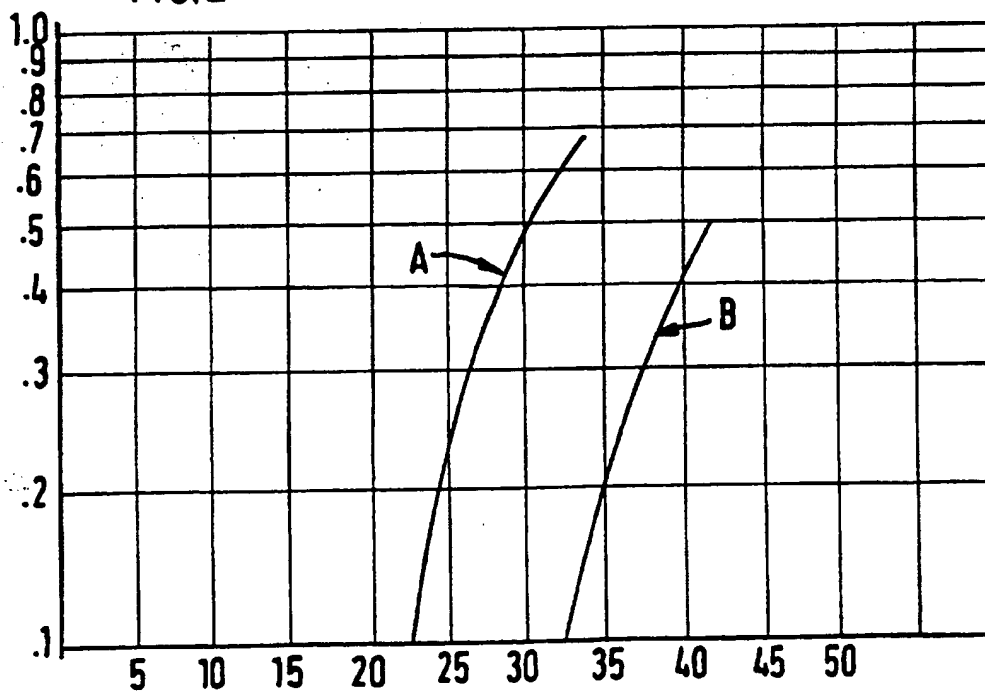


FIG. 2





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EUROPEAN SEARCH REPORT

Application Number

EP 87 20 2087

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	GB-A-1 183 564 (THE DOW CHEMICAL) * Claims 1-4; page 2, lines 46-49 *	1	C 07 C 37/20 C 07 C 39/16 B 01 J 31/10
A	FR-A-1 253 192 (CIBA) * Claim 1; points 1-4; page 2, column 1, lines 21-26, 35-41 *	1	
A	CHEMICAL ABSTRACTS, vol. 82, no. 18, 5th May 1975, page 13, abstract no. 112410h, Columbus, Ohio, US; & JP-A-74 20 565 (SHOWA DENKO K.K.) 25-05-1974	1	
A	CHEMICAL ABSTRACTS, vol. 96, no. 12, 22nd March 1982, page 10, abstract no. 86122h, Columbus, Ohio, US; & JP-A-81 142 227 (MITSUBISHI CHEMICAL INDUSTRIES CO., LTD) 06-11-1981	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 07 C 37/00 C 07 C 39/00 B 01 J 31/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 04-02-1988	Examiner KLAG M.J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document	

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